

CAST IRON MATERIAL

The invention relates to a cast iron material with graphite flakes, which is particularly suitable for producing brake discs, lightweight and heavyweight engine blocks and cylinder heads.

Cast iron with graphite flakes (grey cast iron) is a preferred construction material owing to its good machinability and very advantageous casting properties combined with a low risk of the occurrence of concealed defects. Blocks for internal combustion engines are therefore typically cast from cast iron materials of the type in question.

The requirements already made nowadays on the tensile strength of the material have reached the limits of problem-free applicability of conventional grey cast iron, however. This is due to the fact that, on the one hand, increased capacities, for example in the casting of internal combustion engines, are demanded and, on the other hand, that lightweight construction is a central aim of modern cast constructions. Making the situation more difficult is the fact that users are demanding not only higher tensile strength, of as a rule more than 300 MPa, but also the optimisation of other properties, such as high thermal conductivity, high resistance to thermo-mechanical fatigue and high resistance to frictional wear and sliding abrasion. The quality of the casting result is also subject to strict tests.

The requirements with respect to high tensile strengths can basically be satisfied by reducing the carbon and silicon contents or the degree of saturation and by alloying Cr, Cu, Ni, Mn or Mo up to a total content of the elements added by alloying of about 2%. The resistance to thermo-mechanical fatigue may also be set sufficiently high in this way.

However, said measures lead to a considerable reduction in the casting characteristic and the self feeding capacity of the processed cast iron material. The risk of concealed defects and partially carbidic solidification (edge hardness) occurring increases. At the same time the machinability of the material is considerably impaired. In industrial production reject rates of up to 30% must therefore be accepted for the increase in tensile strength and resistance to thermo-mechanical fatigue attained with said measures.

The demand for high thermal conductivity cannot, however, be met by reducing the carbon and silicon contents or the degree of saturation, or alloying with specific alloy elements since the thermal conductivity of grey cast iron is a function of the quantity of graphite contained in the casting, as is well known, and decreases as the quantities of graphite become smaller. The elements added by alloying also basically lead to a reduction in thermal conductivity.

The latter is particularly noticeable if efficient brake discs are to be cast from an appropriately alloyed material having relatively high strengths.

Owing to the segregation behaviour of these elements, alloying with carbide-forming elements, such as Cr and Mo, leads to the formation of undesirable complex carbides even if it takes place within theoretical limits for the solubility of these elements (rule of thumb: atomic radius of the respective element $< 1.15 \times$ atomic radius Fe). Apart from the fact that these carbides are "waste products" with adverse effects on the machinability, this has the fundamental drawback that if cast material that is produced in the casting operation is re-used in recirculation, the entropy of the entire system of the circuit is increased.

When recycling the material re-used in recirculation, the carbides in particular are, as a rule, not completely destroyed. Instead they are retained as what are referred to as clusters which form carbides again when they solidify. As a consequence of renewed alloying with the respectively stipulated quantities of chromium and molybdenum, new carbides are formed. As a result, this process of enrichment of the processed cast material with carbides leads to a slow, but unavoidable, increase in unusable chromium and molybdenum which ends in a creeping deterioration in the properties of the cast material. As a consequence of the fact that the segregated elements affect the temperature of the eutectic equilibrium in the Fe-C-X system in different ways and the inactive non-metallic phases also present in the melt are likewise subjected to the process of creeping increase, feared "inverse chill" casting defects can occur in the casting operation in extreme cases.

In addition to the above-mentioned prior art, a cast iron material is known from EP 1 213 071 A2 for producing

camshafts which (in % by weight) comprises 3.5 to 3.7% C, 0.9 to 1.1% Si, up to 1% Mn and lanthanum that is not bound to sulphur at a content of 0.02 to 0.05% and may optionally contain 0.3 to 0.6% Cr, 0.1 to 1.0% Cu, 0.3 to 0.6% Mo and 0.02 to 0.05% Ti. Lanthanum is added to the known material with the aim of increasing the hardness of the material and bringing about grain refining that improves the tribological behaviour. The properties of an alloy with this composition have been discussed in detail in EP 1 213 071 A2 using an embodiment which comprised (in % by weight) 3.69% C, 0.95% Si, 0.05% La, 0.029% S, 0.0035% O, 0.29% Mn, 0.5% Cr, 0.2% Cu, 0.51% Mo and 0.022% Ti.

A further example of a cast iron material with graphite flakes is known from EP 1 004 789 A1. This material is used for producing brake discs which are distinguished by increased service life. For this purpose, the cast material known from EP 1 004 789 A1 contains, in % by weight, 3.9 to 4.2% C, 0.7 to 1.2% Si, up to 0.02% P, up to 0.02% S and up to 0.05% Al. The known material may also have Mn, V, Cu and Cr contents, wherein the total fraction of these alloy elements should not exceed 1.6%. A brake disc produced from a material of this type is distinguished by particularly high thermal conductivity combined with good toughness. The known alloy has been specifically tested with the aid of an embodiment which contained (in % by weight) 4.1% C, 1.0% Si, 0.02% P, 0.03% S, 0.3% Mn, 0.01% V, 0.4% Cu, 0.3% Mo and 0.015% Al.

Starting from the above described prior art, the object of the invention was to create an alloy concept which easily allows the respective optimum properties to be adjusted for

a wide product range by varying the contents of the respective alloy components.

This object is achieved according to the invention by a cast iron material with graphite flakes, with the following composition (in % by weight):

C: 3.4 to 4.1%,
 Si: 0.9 to 1.4%,
 Mn: 0.4 to 0.7%,
 Cu: 0.4 to 0.6%,
 S: 0.01 to 0.04%,
 O₂: 0.003 to 0.007%,
 P: ≤ 0.04%,

with the remainder comprising Fe and unavoidable impurities,

wherein the composition can also optionally contain one or more of the following elements:

Mo: 0.15 to 0.45%,
 La: 0.005 to 0.02%,
 Sr: 0.0005 to 0.01%,
 V: 0.005 to 0.1%,
 Ni: 0.05 to 0.8%,
 Sn: 0.05 to 0.15%,
 N: 0.05 to 0.08%

and $0.85\% \leq S_c \leq 1.05\%$ applies to the degree of saturation $S_c = C\%/4.26 - 0.3 * (Si\% + P\%)$ (C%: respective C content, Si%: respective Si content, P%: respective P content), and $1.97\% \leq MEG \leq 2.07\%$ applies to the respective quantity $\%MEG = 2.25\% - 0.2 Si\%$ (Si%: respective Si content).

The invention provides an Fe-C-Si-X cast alloy which, in particular, has a combination of properties which is optimised both with respect to its strength and with respect to its thermal conductivity and pourability and in which the risk of a creeping decrease in the good properties occurring in the practical casting operation is reduced to a minimum.

Cast iron material according to the invention is largely free from undesirable or unnecessary elements and by-products. Thus the sulphur and oxygen contents are of such a size that they no longer have a disruptive influence on the properties of the iron material. As a result, the iron lattice is purified and contains sufficient free capacity for absorbing necessary foreign atoms. Minimum oxygen and sulphur contents are also stipulated as the two elements serve as building blocks for the formation of crystal nuclei.

By adhering to the adjustment rules stipulated according to the invention for the degree of saturation and the quantity of eutectic graphite, the carbon and silicon contents are such that, even with a comparatively wide variation in the degree of saturation S_c , the eutectic quantity of graphite MEG is high.

The quantity of eutectic graphite MEG present in the cast material according to the invention exceeds considerably that of normal cast iron. The MEG value thereof is typically only about 1.85% by weight. In the cast material according to the invention a volume fraction that is higher by 10% to 20% is thus available. A decisive advantage of the cast iron material according to the invention compared

with conventional iron material lies in this excess. Thus material according to the invention has a far superior self feeding capacity for the purpose of balancing out the shrinkage in the iron with expansion of the graphite, compared with conventional cast material. In the casting operation in practice this property leads to a clear increase in the reliability with which high quality cast products are produced.

When producing a cast material according to the invention the reducing melt treatment by seeding should be strongly oriented toward the respective level of the oxygen and/or sulphur contents.

As alloy elements the invention provide elements of which the atomic radius does not differ too greatly from that of iron. The difference is preferably up to a maximum of 2%. The alloy elements should not be strong carbide formers and should not segregate directly. According to the invention it is therefore provided that, if required, copper, nickel, manganese or molybdenum are added by alloying to the iron material in order to adjust its respectively required properties. Tin, of which the atomic radius is up to 50% greater than that of iron, may also be added for this purpose.

Accordingly cast iron material according to the invention contains copper in quantities of 0.4% by weight to 0.6% by weight in order to promote the formation of pearlite without adverse effects on the desired high degree of graphitisation. A further positive effect of the presence of Cu lies in the fact that segregation directions are formed on this element. When producing lighter cast parts,

such as lightweight engine blocks, it has proven to be advantageous if the range of Cu contents is limited to 0.45 to 0.55 in order to achieve these effects.

By way of addition the alloy according to the invention may also contain nickel in amounts of 0.05 to 0.8% by weight, preferably 0.05 to 0.7% by weight. Nitrogen contents of 0.05 to 0.08% by weight can also be provided in combination with Ni or on their own. The two alloy elements ensure that high strengths are obtained in the finished cast part even in the event of partial pearlite breakdown. Ni and N are therefore present in the iron material according to the invention in combination or singly, preferably in particular if cast parts are produced which, owing to their shaping or mass, cool slowly with the danger of the pearlite breaking down. The rule in this case should be that the Ni and/or N contents are higher, the greater the modulus of the respective cast part.

The technical term "modulus" in this case designates the ratio of cast part volume to heat-emitting area, for which "cm" is usually used as the unit of measurement.

Mn contents in the range of 0.4% by weight to 0.7% by weight likewise assist the formation of pearlite. Manganese is added in particular, however, to form segregation directions on manganese. To produce lighter cast parts that cool more quickly, the Mn contents can be limited to the range of 0.45 to 0.65% by weight to achieve this effect.

The maximum phosphorus content is limited to 0.04% by weight to minimise the formation of phosphite eutecticum which would be harmful to the toughness of the material.

The sulphur content should also be limited to a maximum of 0.04% by weight to avoid sulphide formations for this reason. If Cer is present the contents, provided according to the invention, of at least 0.1% by weight are used for nucleation which leads to superfinely distributed oxysulphides. The following rule can be applied: if Ce is present, the Ce content should be adjusted so as to be higher, the greater the respective S content. The oxysulphides formed by Cer in conjunction with sulphur promote the formation of graphite and bring about an increase in the strength and hardness of the material without reducing the toughness thereof.

Mo can be added to the cast iron material according to the invention in amounts of 0.15% by weight to 0.45% by weight to block displacement movements by diffusion from the iron lattice in the event of thermal stress and consequently to prevent the introduction of cracking. The reliability with which the properties, established by the addition of Mo, of the material according to the invention are achieved may be increased in that the upper limit of the Mo content is restricted to 0.35% by weight and the lower limit raised to 0.2% by weight respectively.

Tin contents, which are 0.05% by weight to 0.15% by weight, lead, with longer residence time of the cast part in the mould, to the formation of a micro segregation zone around the graphite flakes and prevent diffusion of carbon from the graphite and into the basic matrix.

Addition of strontium promotes nucleation and development of a structure that is advantageous with respect to the desired properties. At least 0.0005% by weight Sr are

required to reliably achieve this purpose. A positive effect can no longer be ascertained with contents of more than 0.01% by weight on the other hand. In particular in the case of larger cast parts in which the strength is particularly important, a particularly positive effect is established if Sr is present in amounts of 0.0005 to 0.002% by weight.

Lanthanum contents in the range of 0.005 to 0.02% by weight have a favourable effect on the pourability of the cast alloy according to the invention and promote the hardness of the material and its tribological behaviour by inducing grain refining.

If necessary vanadium is added to the alloy according to the invention in order to increase the hardness and tensile strength of the material. Vanadium alloys the cementite of the pearlite and leads to the formation of shorter, rounded flakes in the graphite flakes with the result that the hardness and toughness increase. If vanadium is added to an alloy according to the invention for this purpose, it can be done as a function of the modulus of the respective component in order to reliably attain the desired degree of success. The V content should increase with increasing thickness in this case. Thus practical tests have shown that optimum cast part properties are established if with a modulus of the respective cast part of 0.25 to 0.65 cm the V content is 0.025 to 0.035% by weight, with a modulus of 0.65 to 1.2 cm the V content is >0.035% to 0.065% by weight and with a modulus larger than 1.2 cm the V content is more than 0.055 to 0.1% by weight. The solubility limit is exceeded with contents according to the invention of more than 0.1% by weight.

A variant of the alloy according to the invention that is particularly suitable for producing brake discs is characterised in that its carbon contents are in the range of 3.8 to 4.1 % by weight. The relatively high carbon content leads to strengths which are in the range of 150 to 200 MPa. At the same time cast parts produced from the alloys with this type of composition have high thermal conductivity combined with a high level of toughness. The silicon content is preferably in the range of 0.9 to 1.2% by weight for the same purpose.

For casting cast parts in which a high strength combined with good thermal conductivity is to the fore, a further variant of the invention provides that the C content is in the range of 3.4 to 3.8% by weight, in particular 3.4 to 3.6% by weight.

Tests have shown that cast iron material according to the invention with a composition of this type has high strengths which are regularly more than 300 MPa in the cast state.

When casting thick-walled cast parts, it is also advantageous if the Si content of the alloy is 1.15 to 1.4% by weight, in particular 1.2 to 1.4% by weight, in order to meet the danger during casting of re-oxidation with reduced C contents.

The oxygen contents of a cast iron alloy according to the invention have particular significance. Speed and extent of nucleation are controlled by the O₂ content. Thus an increase in the oxygen content leads to rapid particle

growth, while lower oxygen contents result in less growth. These effects are achieved with O_2 contents which are in the range of 30 to 70 ppm. If brake discs or similarly configured components are produced from the alloy according to the invention, optimum structures may be obtained via the oxygen content such that the oxygen contents are limited to 30 to 40 ppm. With thin-walled cast parts, such as light engine blocks or the like, with a modulus of 0.1 to 0.4 cm, high O_2 contents of 50 to 70 ppm have proven to be advantageous as they promote fast grain growth within the respective short cooling time. In the case of thick-walled components with moduli in the range of 0.4 to 1 cm, for example heavy engine blocks, optimised structural properties are achieved if the O_2 content is 40 to 60 ppm. When casting cast parts with a complex shape, such as cylinder heads, with a modulus in the range of 1 to 2.5 cm, on the other hand, grain growth that is optimised with respect to the properties demanded of these components is achieved if the O_2 content of the alloy according to the invention is in the range of 30 to 50 ppm.

The high tensile strengths of a cast material according to the invention may be particularly reliably ensured in that in the cast state more than 50% of the oxygen contained in the cast iron material according to the invention is in the form of a type of oxide of which the starting temperature of the reduction with oxygen is above 1,700 K.

In addition to the improved strength, thermal conductivity, toughness and machinability cast iron material according to the invention also has good corrosion resistance. As a result of this specific combination of properties, cast iron material according to the invention is particularly

suitable for producing brake discs and engine blocks or cylinder heads for internal combustion engines. In particular the high tensile strengths combined with good pourability, machinability and high thermal conductivity make the material according to the invention particularly suitable for use as material for producing blocks for modern diesel engines, in which extremely high pressure loads occur in the region of the combustion chamber during the course of the combustion process.

The properties of cast iron material according to the invention have been proven in a large number of examples.

Thus HGV brake discs have been cast from cast iron alloys according to the invention with the compositions B1 to B7 given in Table 1a in % by weight, the Sc value, %MEG value, tensile strength R_m and Brinell hardness HB of which are given in Table 1b. Table 1b also contains an evaluation of the structure of the products obtained in each case.

It has been found that the HGV brake discs cast from the alloys given in Table 1a have tensile strengths in the region of 160 to 230 MPa. The hardness values are in the range of 147 to 220 in this case, so the brake discs have good wear resistance in addition to high strengths. They also have outstanding thermal conductivity, so they can reliably absorb and discharge the forces acting on them even in the case of high loads.

Table 2a gives the contents of C, Si, S, Mn, Cu, V, Mo, Sn and Ni for alloys D1 to D5 of cast iron materials according to the invention, from which thin-walled car engine blocks with a modulus of 0.7 to 0.8 cm have been cast. The

relevant alloys D1 to D6 also contained 60 ppm by weight O₂ and 0.01% by weight La in each case. Table 2b contains the associated values %MEG, SC, tensile strength R_m and Brinell hardness HB averaged over various measuring points in each case, as well as an evaluation of the structure.

Table 3a gives the contents of C, Si, S, Mn, Cu, V, Mo, Sn and Ni for alloys Z1 to Z6 of cast iron materials according to the invention, from which cylinder heads weighing 100 kg (alloys Z1 to Z4) and 400 kg (alloys Z5, Z6) have been cast. The modulus of the 100 kg cylinder heads were between 2.5 and 3 cm while the modulus of the cylinder heads weighing 400 kg was 1 cm. The relevant alloys Z1 to Z6 also contained 40 ppm by weight O₂ and 0.01% by weight La. Table 3b contains the associated values %MEG and SC, tensile strength R_m and Brinell hardness HB and an evaluation of the structure.

Finally, a heavy crankcase was cast from a cast iron alloy according to the invention consisting of (in % by weight) 3.6% C, 1.35% Si, 0.1% Sn, 0.5% Mn, 0.5% Cu, 0.01% V, 0.2% Mo, 40 ppm by weight O₂ and 0.03% S, with the remainder being iron and unavoidable impurities. The SC value of the alloy was 0.93 and its %MEG value was 1.98. The finished case had a tensile strength R_m of 320 MPa and a finely structured pearlitic construction.

The invention thus provides a cast iron material which has a superior property spectrum which can be varied over a wide range. The material according to the invention is characterised by particularly good machinability. Its high tensile strength allows known cast constructions, which previously had been produced only from conventional grey

cast iron, to be produced with higher strengths without expensive restructuring being necessary.

	C	Si	S	Mn	Cu	V	Mo	O ₂	La	Sn
B 1	3.9 0	0.9 7	0.05 0	0.4 8	0.5 2	0.09 1	0.4 3	0.003 5	0.0 1	
B 2	3.9 6	1.0 2	0.02 8	0.5 2	0.5 1	0.08 8	0.4 7	0.003 5	0.0 1	
B 3	3.9 5	1.1 4	0.03 7	0.5 3	0.5 4	0.09 3	0.4 0	0.003 5	0.0 1	
B 4	4.0 7	1.0 8	0.04 3	0.4 8	0.4 8	0.08 3	0.0 2	0.003 5	0.0 1	
B 5	4.0 9	1.2 2	0.02 7	0.4 7	0.5 0	0.09 8	0.4 1	0.003 5	0.0 1	
B 6	3.9 9	0.9 5	0.02 0	0.5 2	0.5 6	0.00 6	0.2 7	0.003 5	0.0 1	
B 7	3.9 4	1.0 5	0.02 6	0.5 5	0.6 0	0.00 5	0.2 9	0.003 5	0.0 1	0.1 0

Remainder iron and unavoidable impurities

Table 1a

	SC	%MEG	Rm	HB	Structure
B1	0.98	2.056	191.0	207	Finely structured pearlite, Carbide < 1%
B2	1.00	2.046	207.3	210	Finely structured pearlite
B3	1.01	2.022	231.2	201	Finely structured pearlite, Carbide < 1%
B4	1.03	2.034	172.1	186	Finely structured pearlite
B5	1.05	2.006	143.9	171	Finely structured pearlite, Centre ferrite
B6	1.00	2.060	162.5	147	Finely structured pearlite
B7	1.00	2.040	185.2	173	Finely structured pearlite, Carbide < 1%

Table 1b

	C	Si	S	Mn	Cu	V	Mo	Sn	Ni
D1	3.67	1.24	0.026	0.57	0.69	0.005	0.30	0.09	0.63
D2	3.60	1.20	0.031	0.48	0.50	0.044	0.19	0.01	
D3	3.60	1.21	0.026	0.48	0.49	0.044	0.19	0.01	
D4	3.48	1.22	0.038	0.48	0.51	0.045	0.19	0.01	
D5	3.52	1.34	0.037	0.52	0.46	0.043	0.20	0.01	

Remainder iron and unavoidable impurities

Table 2a

	SC	%MEG	Rm	HB	Structure
D1	0.943	2.002	224.9	222	Finely structured pearlite
D2	0.923	2.010	252	222	Finely structured pearlite
D3	0.923	2.008	244.7	185	Finely structured pearlite
D4	0.893	2.006	290.4	189	Finely structured pearlite
D5	0.912	1.982	277.3	201	Finely structured pearlite

Table 2b

	C	Si	S	Mn	Cu	V	Mo	Sn	Ni
Z1	3.45	1.16	0.023	0.53	0.60	0.045	0.34		
Z2	3.56	1.18	0.010	0.51	0.66	0.005	0.19		
Z3	3.53	1.09	0.028	0.54	0.52	0.036	0.29		
Z4	3.57	1.23	0.024	0.60	0.56	0.045	0.29	0.10	
Z5	3.51	1.19	0.027	0.57	0.59	0.039	0.30		
Z6	3.38	1.12	0.025	0.57	0.68	0.049	0.31		0.65

Remainder iron and unavoidable impurities

Table 3a

	SC	%MEG	Rm	HB	Structure
Z1	2.018	0.88	350.0	229	Finely structured pearlite
Z2	2.014	0.91	237.1	186	Finely structured pearlite
Z3	2.032	0.90	210.0	187	Finely structured pearlite
Z4	2.004	0.92	281.5	215	Finely structured pearlite
Z5	2.012	0.90	295.3	195	Finely structured pearlite
Z6	2.026	0.86	313.2	205	Finely structured pearlite

Table 3b